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(54) Process of producing graphite fiber

(57) A process of producing graphite fiber comprising a generation of the fiber by chemical vapor deposition method using organic metal compound which includes catalyst metal as raw material, characterized to use less reactive substance as a substrate and previously to stick carbon or metal at specific position of the substrate. And a process of producing graphite fibers by chemical vapor deposition method comprising an use of fine particles of nickel, iron or cobalt as catalyst and an use of organic compound as raw material, characterized generating the fibers at the range of temperature between 650°C and 800°C.

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generates graphite fiber on th substrate by said reaction. Cobalt, nickel, iron and these alloy are used as metal which acts as the catalyst. In this invention, the following compounds can be used as the raw material. That is, th organic compound having an adequate vapor pressure for CVD, or the metal-organic compound including said metals which act as catalyst can be used. Concretely, organic compounds not including metal such as orthomethyldiallylketone family or it's derivatives, phthalocyanine compounds and metallocene compounds which includes metal catalyst can be preferably mentioned, however the scope of this invention is not intended to be limited to them. The said less reactive substance which can be used as the substrate in this invention is the substance which does not participate in CVD reaction of this invention and also does not react with metal at reacting temperature, and concretely is quartz, alumina, oxidized silicon, or the like. And on the surface of said substrate carbon or metal is stuck, then the graphite fiber is generated at the said stuck point alone. In the expression of "carbon or metal" of this invention, the term of "metal" indicates a transition metal and preferably indicates a metal of iron or platinum family, and concretely cobalt, platinum or the like can be mentioned. It is not necessarily to agree the kind of metal included as a component in the raw material organic metal compound with the kind of metal stuck on the surface of substrate.

In this invention, the graphite fiber is produced on the substrate on which carbon or metal is stuck by using vacuum evaporation or CVD method. Although the heat treatment temperature is different by the vapor pressure of raw material, for instance is about from 50°C to 400°C. And, the substrate must be heated, but the necessary temperature is different by the kind of raw material and generally is concentrated about within the range from 600°C to 1000°C. And especially preferred within the range from 700°C to 850°C. Desirable atmosphere of the reacting space is in a condition of inert gas e.g. argon, nitrogen or the like and at a pressure of under 1atm. or the less, or in a vacuum condition.

At the surface area of substrate on which the generation of graphite fiber is intended, carbon or metal is previously stuck. As the method for sticking previously carbon or metal, following methods can be mentioned. That is, after preparing the layer of photo resist resin on the surface of substrate, necessary pattern is written by photo-lithographical technique, then heated, carbonized and carbon is stuck on the surface of substrate. Or, after metal layer is vaporized on the surface of substrate, and the obtained metal layer is processed to form the pattern of narrower lines than 1μm width, or dotted pattern or other necessary pattern by photo-lithographical technique. In the case of the metal thin layer, there is no limitation on thickness, however, in the case of carbon thin layer, the desirable thickness is thinner than 50nm. If the pattern is like a particle, in the case of carbon, the size is desirably smaller than 50nm in diameter.

Further, the following preparation method of the substrate can be mentioned. The thin layer of carbon or metal and the thin layer of less reactive substance is stacked mutually. And a part of outer surface layer made by less reactive substance is removed so as to partially expose the layer of carbon or metal. By using said substrate having stacked layer the following effect can be expected. That is, if the applied carbon or metal has electrical conductivity, since the graphite fiber is generated at the inner layer of carbon or metal, the generated graphite fiber is electrically connected.

In this invention, the case which uses nickel metal as the catalyst is disclosed in detail below. The use of fine particles of nickel as the metal catalyst, promises the possibility of producing graphite fiber without using organic metal compound as the raw materials and by mild reacting condition of 650°C to 800°C.

The important point of this invention is explained as follows. That is, in this invention, the process of producing graphite fibers is composed by using fine particles of nickel as a catalyst, using organic metal compound as a raw material and producing graphite fibers by means of CVD method, wherein characterised by generating graphite fibers on fin particles of nickel within the range of temperature between 650°C and 800°C. And, as the fine particles of nickel catalyst, it is desirable to use the fine particles of nickel which is prepared in vacuum or in non-oxidation atmosphere by heat treating the thin film of nickel formed on the surface of substrate and by coalesing and granulating it on the substrate. And to carry out easily the coalescence and granulation of nickel,it is desirable to prefer the less nickel adhesive substance as the substrate.

Namely, in this invention, fine particles of nickel metal are used as the catalyst for producing graphite fibers, and the fine particles of nickel metal are used by being dispersed on the surface of substrate.

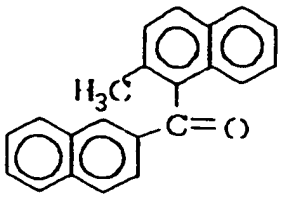
Furtheremore, when the metal-organic compound are used as the raw material, it is possible to produce the fibers which involve large amount of metal.

The process of producing graphite fiber of this invention is schematically illustrated with the accompanying drawing. In figure 1, nickel evaporated film "b" is prepared on the surface of substrate "a" (i), then is heated at the temperature of 700°C around. Since nickel is less adhesive with the substrate, the nickel evaporated film "b" is scattered as nickel fine particles "c" on the substrate (ii). The said fine particles of nickel "c" scattered on the substrate are used as the catalyst, and crystals of graphite are generated by means of CVD method. The crystals of graphite generated at the nickel fine particles "c" scattered position and the graphite fibers are produced (iii). Consequently, in this invention, it is possible to produce the graphite fiber at desirable position by the selective positioning of the nickel metal fine particles on the surface of substrate.

In this invention, it is necessary to disperse the nickel metal fine particles. To disperse the nickel metal fine particles, the substance which is less adhesive with nickel metal is preferred as the substrate and nickel film is prepared on the surface of said substrate. Since the condensing force of nickel itself is stronger than the adhesiv force of nickel with the substrate, when it is heat treated nickel is granulated and dispersed over the surface of substrate. In this invention,

erated by reaction on the inner surface of reacting tube. Said liner tube 41 must be changed to clean one by every reaction. Raw material 1 for CVD method is inserted into container 2 and set into liner tube, and the amount of vaporization is controlled by the temperature of the electric furnace 6. The temperatur of substrate 3 set in the same liner tube 41 is controlled by the electric furnace 5.

In this EXAMPLE, 2-methyl1,2'-naphthylketone indicated by following formula is used as the raw material.



The substrate used in this Example is quartz glass, and nickel evaporated film of 5nm thickness is prepared on it. Highly purified argon gas can be supplied to the reacting tube trough flow controller 7. To the evacuating side of the reacting tube an evacuate equipment 9 is installed trough a valve 8 so as to control the pressure of reacting tube. The temperature of the part in which the raw material is placed, is fixed at 100°C. Said temperature is fixed for the purpose to evaporate the raw material at adequate pressure. And the temperature of the part in which the substrate is placed is fixed at 700°C. The nickel evaporated film on the surface of substrate can be granulated at said temperature. Highly purified argon gas is supplied by flow rate of 300cc/minutes and reacted for 3 hours at 1 atom. After the reaction, the generation of graphite fiber involving fine particles of nickel can be observed. The obtained specimen is measured by Raman scattering spectrum. According to the resulting chart of spectrum shown in figure 3, the obtained spectrum has an unique feature of crystalline graphite, and the generation of graphite substance is confirmed. Further, by the Scanning Electron Microscope (SEM) observation the generation of many fibrous substance is confirmed. The fibrous substance is observed by Transmission Electron Microscope (TEM), it is understood that the each fiber is hollow, partially involves fine particles of nickel and has a structure of winding like as a concentric column. Said structure is called as carbon nano-tube. So, hereafter the term of carbon nano-tube is used in this invention.

The reason why above mentioned reaction is occurred is investigated by the inventors, and it become clear that the evaporated nickel film is concentrated like small islands during the interval of temperature rising to the reacting temperature, and the concentrated fine particles of nickel become the catalyst of carbon nano-tube generation.

The temperature of the substrate arranged place, that is, the reacting temperature is varied from 300°C to 1000°C and the generation of carbon nano-tube is observed. It is found out that the adequate temperature for the generation of carbon nano-tube is limited within the range between 650°C to 800°C.

The experiments to reduce the pressure of reacting tube to the lower level than 1atm. are carried out, and it is recognized that the carbon nano-tube can be generated at the pressure of 0.01atm. as well as 1atm. condition.

EXAMPLE 2.

Example 2 is concretely illustrated with reference to figure 5.

Figure 5 is a schematic view of an apparatus used in Example 2. Quartz reacting tube 4 can be evacuated to the pressure level of 10^{-6}Pa by using evacuate line 29 with turbo molecular pump. Raw material 1 and substrate 3 is set in this quartz reacting tube. A kind of raw material is same to that of Example 1, and also the same substrate is used. After the raw material 1 and the substrate 3 are set, inside of reacting tube is evacuated to 10^{-5}Pa by using evacuate line 29. Then, continuously evacuating, the temperature of substrate 3 is risen to 700°C and the temperature of raw material is risen to 100°C. Raw material is evaporated and reacted on substrate 3. Product by the reaction is precipitated at the low temperature part of reacting tube 4. The colour of precipitated product is white or light yellow. After the reaction, the temperature of electric furnace is cooled down and the substrate is checked. Same as to Example 1, the generation of carbon nano-tube is confirmed. The temperature of the place where the substrate is set, namely the reacting temperature is varied from 300°C to 1000°C, and it is found out that the adequate temperature to generate carbon nano-tube is limited within the range between 650°C and 800°C. Raw material 1 and substrate 3 can be heated to the intended temperature by using electric furnace like as to Example 1.

EXAMPLE 3

Same apparatus to the Example 2 is used except using the substrat having patterned nickel evaporated thin film

terns can be understood to have a characteristic of fine particles. Substrates having those patterns are used for the experiments to generate graphite fiber. On the bigger pattern, the generation of plural graphite fibers are observed, however, on the small pattern a single fiber is generated. And by this phenomenon, it is recognized that the pattern on quartz gives an opportunity of generation of fiber.

EXAMPLE 8.

Quartz is used as a substrate, and photo resist resin (AZ-1400) is coated by 0.2μm thickness on the substrate, then the pattern of 1μm width is formed by using photo-lithographical technique. This resist pattern on quartz is heated and carbonized in argon gas flow at 700°C, and experiments to generate graphite fiber are carried out. And the generation of fiber is observed only on the carbonized resist. However, it is found out that the too thick resist layer prevent the growth of fiber. For the generation of good fiber is preferably performed on the resist of thinner thickness than 1nm. Fibers do not generate on the area where quartz is exposed.

EXAMPLE 9.

As the another example of this invention, the substrate of a different construction is used.

Figure 6(a) is a cross-sectional view illustrating the construction of substrate used in this Example. Cobalt metal layer of 250nm thickness is evaporated on a quartz plate 31, and on the said layer quartz layer 33 of 8nm is formed by using plasma CVD method. Quartz layer 33 is partially removed by photo-lithographical technique, and the inner cobalt layer 32 is exposed.

By using said substrate, experiments are carried out by using same process to Example 5, and the generation of graphite fiber is observed on the exposed cobalt surface. However, on the surface of quartz layer nothing is generated. This state is schematically illustrated in figure 6(b).

EXAMPLE 10.

Figure 7 is a illustration of construction of different substrate. In figure 7, metal cobalt layer 32 of 250nm thickness is evaporated on quartz plate 31, and on this layer quartz layer of 80nm thickness is formed by plasma CVD technique. The quartz layer and the cobalt layer 32 are partially removed by photo-lithographical technique, and the bottom quartz plate surface is exposed. That is, the metal is exposed at the section of layer put between quartz layers.

By using said substrate, experiments are carried out by using same process to Example 5, and the generation of graphite fiber is observed on the exposed cobalt thin surface put between quartz layers. However, on the surface of quartz layer nothing is generated. This state is schematically illustrated in figure 7(b).

As above mentioned, this invention provides the process of producing graphite fiber locally, and by this process it is possible to control the position where fibers generate by submicron level precision.

Claims

1. A process of producing graphite fiber, comprising a generation of the fiber by chemical vapor deposition method using metal-organic compound which includes catalyst metal as raw material, characterized using less reactive substance as a substrate and previously sticking carbon or metal at specific position of the substrate surface.

2. The process of producing graphite fiber of claim 1, wherein the state of carbon or metal to be previously stuck to the substrate is thin film or fine particles.

3. The process of producing graphite fiber of claim 1, wherein the thickness of previously stuck carbon or metal is thinner than 50nm.

4. The process of producing graphite fiber of claim 1, wherein the metal to be previously stuck to the substrate is a same metal to that of included in the organic metal compound or different metal not form a stoichiometrically stabilized metal carbide compound.

5. The process of producing graphite fiber of claim 1, wherein the substrate is a laminated compound of carbon or metal layer previously stuck to the substrate and the layer of less reactive substance or the like compose the substrate, and the carbon or metal layer is exposed by partially removing the layer of less reactive substance of uter surface of this substrat .

6. The process of producing graphite fiber of claim 1, wherein the second layer of carbon or metal is partially removed

Figure 1

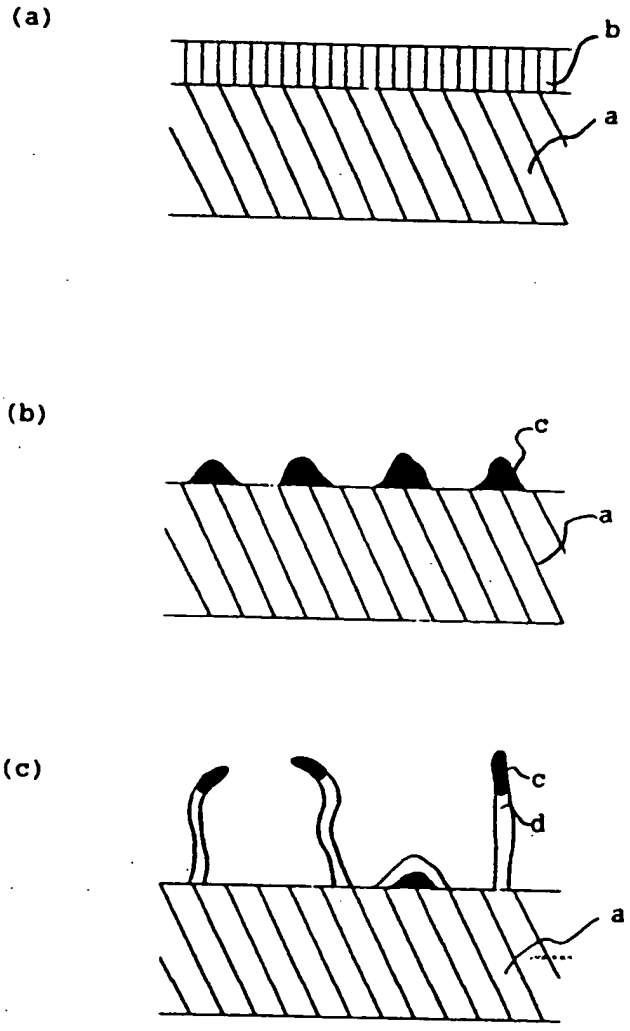


Figure 4

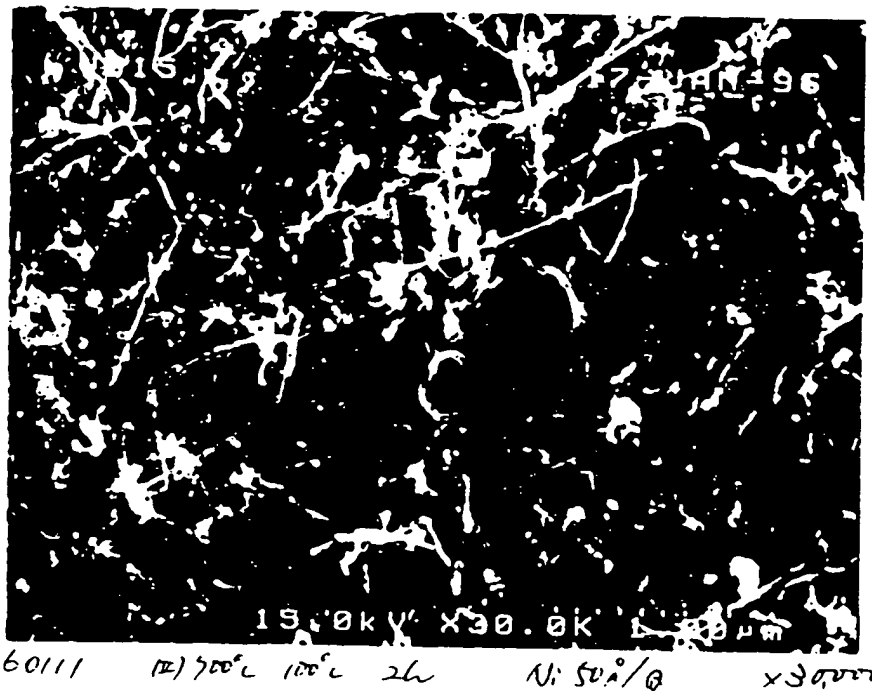


Figure 5

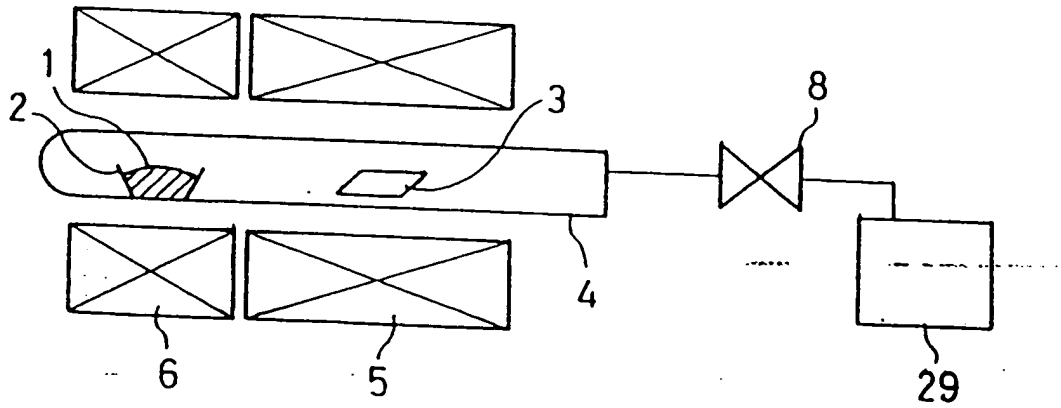
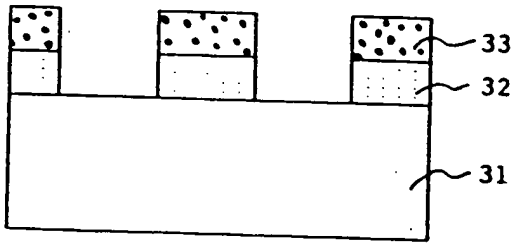


Figure 7

(a)



(b)

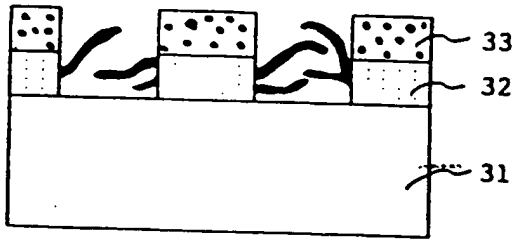


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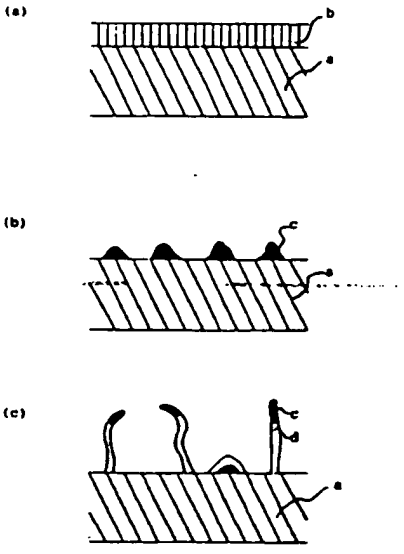
Figure 1



EP 0 758 028 A3